THE ANALYST.

OCTOBER, 1892.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

ON THE DETERMINATION OF OLEIC ACID.

By Otto Hehner.

(*Read at Meeting, June 30th*, 1892.)

Being lately desirous of estimating the amount of olein in butter-fat, and of determining whether the whole of the iodine absorption of butter-fat could be calculated into olein, or whether there was any foundation for the statement made by Koefoed that other still more unsaturated fatty acids were present, I attempted the separation of the lead-salts by means of ether in the usual manner. The method in question was first proposed by Varrentrapp, and afterwards variously modified by Oudemans, Kremel, and Muter; but as these chemists had not the advantage of being able to test the various products by Huebl's Iodine Absorption Method, which sharply distinguishes saturated from unsaturated fatty acids; and as I had previously found that the lead salts of the higher saturated fatty acids were not by any means insoluble in ether, I thought it desirable to submit the method to a critical examination.

Ten grammes of butter-fat were saponified with alcoholic potash, the alcohol driven off, the soap rendered perfectly neutral, and the aqueous solution precipitated with neutral lead acetate. The precipitate was collected, pressed, and air-dried. It was then extracted in a Soxhlet tube with ether. After many hours' extraction, the soluble portion was decomposed with hydrochloric acid in the presence of ether, the ether solution of the fatty acids well washed with water, the ether evaporated in a current of carbonic acid, and the fatty acids dried in that gas till constant in weight. 32·1 per cent. of fatty acids were thus obtained, which showed an iodine absorption of 58·04 per cent.

The extraction of the insoluble lead salts with ether was then continued for some hours, and 3·95 per cent. of dissolved fatty acids were obtained with an iodine absorption of 55·48 per cent. By persistent extraction a third fraction was obtained, amounting to 3·68 per cent., with an iodine figure of 59·18 per cent. The lead-salts which had remained undissolved in ether were then decomposed with hydrochloric acid, and dried in carbonic acid to constant weight. 42·53 per cent. were obtained, with an iodine

absorption of 18·60 per cent. Thus altogether 82·27 per cent. of fatty acids were obtained, a figure which falls short somewhat of the actual quantity present in the sample of butter-fat, but it is almost impossible so to manipulate the sticky lead-precipitates as to avoid some loss.

It is obvious from this experiment, that although the extraction with ether lasted for several days, a complete separation of the salts of the saturated fatty acids from those of the unsaturated ones had not been obtained. The iodine absorption of even the first soluble portion was far too low for pure oleic acid, which is 90·1 per cent., and the saturated fatty acids had evidently dissolved in abundance. It is equally clear that, in spite of the protracted treatment with ether, the remaining lead-salts still included a considerable proportion of unsaturated fatty acids.

The equivalent of the first portion of ether-soluble acids was found to be 256·8, and that of the remaining insoluble acids 254·7.

As these results might have been attributed to the complicated composition of butter-fat, and to the presence on the one hand of unsaturated fatty acids with insoluble lead-salts, or to the solubility of the lead-salts of the lower fatty acids, I made a similar attempt to estimate the olein in a sample of margarine, which had been prepared from animal fats only, and which did not contain more than a mere trace of butter-fat obtained from the milk employed in its manufacture.

The lead-salts were extracted for two days with ether, the residue dried, ground up finely, and once more extracted for some time. The soluble lead-salts thus obtained amounted to 48·1 per cent., and had an iodine absorption of 64·88 per cent., while the insoluble lead-salts furnished 46·0 per cent. of fatty acids, with an iodine absorption of 17·72.

Here no low fatty acids were present that could complicate the result, nor, in all probability, any unsaturated fatty acids with less hydrogen than oleic acid; and yet nothing like pure oleine had been obtained, nor had the whole of the unsaturated fatty acid been removed by the persistent extraction with ether.

The lead-salts from cotton-seed oil dissolved almost completely in ether, and yielded an ether-soluble acid portion with 116·26 iodine absorption. The small portion which was insoluble in ether gave fatty acids with an iodine figure of 35·3. The cotton oil employed absorbed 108·6 per cent. of iodine.

A sample of almond-oil, with an iodine figure of 98·87, also yielded a lead-soap which was almost completely dissolved by ether in a few hours, the soluble portion of the fatty acids absorbing 100·67 and the small insoluble portion 98·71 per cent. of iodine.

From a sample of cocoa-nut oil, which showed an iodine absorption of 8·22 per cent., 63·49 per cent. of acids whose salts were soluble in ether were obtained, and 19·58 per cent. of insoluble acids. The former absorbed 10·49 per cent. of iodine, the latter 0·69. This latter small figure is within the limits of experiment, and it appears as if the olein

of cocoa-nut oil could be completely washed out by abundance of ether from the lead-salt, but nothing like an estimation was evidently possible, as a far larger amount of saturated fatty acids passed into the ether solution than of lead oleate.

These figures show most conclusively to my mind that the method of olein determination, which is founded upon the relative solubilities of the lead-salts in ether is utterly untrustworthy. Neither are the lead-salts of the saturated fatty acids sufficiently insoluble, nor the unsaturated lead-salts so easily soluble as to allow of a separation useful for analytical work. Sometimes the two sources of error may counterbalance each other. Thus in the sample of butter-fat, to which I referred in the beginning of this note, the iodine absorption was 33·32 per cent., corresponding to 38·6 per cent. of olein (assuming that the whole of the iodine absorption was due to olein only), and the soluble portion obtained by lengthy extraction amounted to 39·7 per cent., but this is obviously only a coincidence, as in no case was the iodine absorption of the soluble fractions more than 59 per cent., which figure is only about two-thirds of the iodine absorption of oleic acid. By less protracted extraction, such as the mere shaking out of the lead-precipitate with ether for a short time, a purer olein may possibly be obtained, but a still larger portion of olein than that shown in the above experiments would be left undissolved with the saturated lead-salts.

Since carrying out my experiments my attention has been drawn to an investigation of the Sawarri nut by Lewkowitsch (*Soc. Chem. Ind.* 1890, 845), in which a separation of the lead-salts was also attempted by means of ether, with unsatisfactory results.

I beg to record my obligation to my assistant, Mr. W. P. Skertchley, for carefully carrying out most of the analytical work recorded in this paper.

Discussion.

Mr. A. H. Allen said he had listened, and he was sure that all present had listened, with very great interest to the very important, novel, and suggestive communication which had been made by the President. The subject furnished another illustration of the proverb, "put not your trust in book-makers." It was a most unfortunate thing that a large number of statements which appeared in standard works had no foundation in fact, and got repeated from one book to another to the great detriment of workers. Mr. Hehner had shown the unreliability of the usual process employed for separating oleic acid from acids of the stearic series. They were literally deprived of the only method which had been thought capable of giving anything like a reasonably accurate estimation of the actual proportion of oleic acid in a mixture, and that being the case it remained to be seen what else could be done in this direction. It was possible that a change of solvent might answer. The change from ether to petroleum spirit might effect a sharper separation of the lead oleate from the lead-salts of the saturated acids, and some modification of that sort might be found feasible.

THE DETERMINATION OF CARBON DIOXIDE IN THE AIR OF BUILDINGS.

By Augustus H. Gill, Ph.D.

In the only treatise upon air analysis in the English language, the method given for the determination of carbon dioxide admits of no great accuracy, as results varying 6 per cent. from an average, and 10 per cent. among themselves, would indicate. The writer recommends the following method, which has been in use in his laboratory in almost the present form for fifteen years.

Both methods are those of Pettenkofer,* which consists in bringing a large known volume of air in contact with standard barium hydrate solution.

The bottles used for containing the samples are ordinary green glass gallon or two gallon bottles, holding 4,400 or 8,800 c.c. respectively; they are calibrated with water, by weighing upon scales sensitive to 5 gms., and their capacity marked upon them with a diamond. They may be conveniently transported from place to place in a partitioned basket made for the purpose.

The bellows there suggested (wooden discs joined by a strip of rubber, with no valves) was found troublesome to manipulate, and has given way to one about to be described. The nozzle of an ordinary 9-inch blacksmith's bellows is removed and the opening fitted with a valve opening outward; this is made by tying a bit of chamois skin over a cork which fits over a tube passing into the nozzle opening. By varying the position of the cork, different degrees of tightness of valve are attained. To the other opening of the bellows, closed with its usual valve, is fitted a cork carrying a four-foot piece of $\frac{5}{8}$-inch rubber tubing terminating in a light two-foot brass tube, bent for insertion into the bottles. Instead of the bellows, a small 6-inch fan blower, the driving parts of which are connected by rubber bands to render it noiseless, can be used if it is desired to decrease the bulk of the apparatus.

The bottle is fitted with a rubber stopper, carrying a glass tube, closed by a small unperforated rubber nipple; both the stopper and nipple have been digested with caustic potash and thoroughly washed to remove the superficial zinc oxide.

The air to be tested is drawn into the bottle by means of the bellows, fifteen strokes being taken, sufficing to fill a four litre bottle four times, thus insuring a representative sample. In collecting this sample the atmosphere in the room should be as quiet as possible; care must be exercised to avoid the drafts or the proximity of people.

When used the bottles should be *clean* and *dry*; by clean is understood containing nothing to affect the barium hydrate used. When wet the standard barium hydrate is diluted, and as the whole of it is not used, the determination is lost, unless the amount of water present be accurately known.

* Annalen, 2, Supp. Band, p. 1.

The operation of drying the bottles is by no means as troublesome as it would appear. A small closet heated by steam and provided with suction, enabling a current of hot air to be drawn into the bottles, suffices to dry a dozen bottles in half an hour. The samples are brought into the laboratory, the temperature of which should be a little higher than that of the place where they were taken, and allowed to stand half an hour, or until they have attained its temperature.

50 c.c. of the standard barium hydrate are now run in rapidly from a burette (the tip passing entirely through the tube in the stopper), the nipple replaced, and the solution spread completely over the sides of the bottle while waiting three minutes for the draining of the burette, before reading, unless it be graduated to deliver 50 c.c. The bottle is now placed upon its side, and shaken at intervals for 40–60 minutes, taking care that the whole surface of the bottle is moistened with the solution each time. The time of absorption, ten minutes, recommended in the treatise, is much too short, as the disappearance of the last traces of carbon dioxide is very slow indeed, half an hour in many cases being insufficient.

At the time at which the barium hydrate is added, the temperature and pressure should be noted. At the end of the above period, shake well to insure homogeneity of the solution, remove the cap from the tube, and invert the large bottle quickly over a 50 c.c. glass stoppered bottle, so that the solution shall come in contact with the air as little as possible. Without waiting for the bottle to drain, withdraw a portion of 15 or 25 c.c. with a narrow stemmed spherical bulbed pipette and titrate with sulphuric acid* (1 c.c. equals 1 mgm. CO_2) using rosolic acid as an indicator. The difference between the number of cubic centimetres of standard acid required to neutralize the amount of barium hydrate (*e.g.*, 50 c.c.) before and after absorption, gives the number of milligrams of carbon dioxide present in the bottle.

This is expressed in cubic centimetres under standard conditions, and divided by the capacity of the bottle under standard conditions, and the results reported in parts per 10,000. To reduce the air in the bottle to standard conditions, a hygrometric measurement of the air in the room from which the sample was taken, is necessary. This in ordinary cases is usually omitted, as the object of the investigation is *comparative* results, as regards the efficiency of ventilation, and the rooms in the same building would not vary appreciably in the amount of moisture in the atmosphere. This correction may make a difference of about 0·15 parts per 10,000.

Some of the results obtained by our students by the preceding method are as follows :—

* Sulphuric acid, in distinction to oxalic acid, enables one to estimate the excess of barium hydrate in presence of the suspended barium carbonate, and also of caustic alkali, which is a frequent impurity of commercial barium hydrate. Professor Johnson, in the American edition of *Fresenius' Quantitative Analysis*, calls attention to the fact that the normal alkaline oxalates decompose the alkaline earthy carbonates, so that the reaction continues alkaline if the least trace of soda or potash be present. The sulphuric acid may be prepared by diluting 46·51 c.c. normal sulphuric acid to a litre.

Expressed in parts of CO_2 per 10,000.

Room No. 24.	No. 43.	No. 37.	No. 34.	No. 34.	No. 23.	Outside Air.
5·54	7·34	4·94	5·16	5·53	4·54	3·13
5·59	7·27	4·89	5·12	5·52	4·46	3·09

The subjoined results are interesting as showing rate of vitiation of the air in a well-ventilated lecture room. It is 15 feet high, having a capacity of 24,000 cubic feet, and supplied with 185,000 feet of air per hour, from three flues; 225 students were present.

	Time.	1st Day. Pts. CO_2 in 10,000.	2nd Day.
Before lecture	11.35	3·89	4·54
	12.10	6·07	9·93
	12.20	8·44	10·27
	12.30	11·29	10·43
	12.40	11·38	10·50
	12.50	10·56	10·58
End of lecture	1.00	6·62	7·19
	1.30	3·72	6·10

The following shows the distribution of carbon dioxide in an ordinary theatre:—

	CO_2 per 10,000.
Floor	39·13 pts.
1st Balcony	42·86 „
2nd Balcony	44·72 „
Gallery	48·94 „

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NEUTRALITY.*

By Alfred H. Allen.

The comparatively recent recognition of the true position of hydrogen has probably done much to retard the progress of chemical science, especially with respect to the theory of neutral salts. But perhaps still more injury has been done by the almost universal habit, which existed till a few years ago, of looking at the constitution of all saline compounds from the view of their action on litmus. One of the first things that a student was taught, and still is, in many cases, is that the criterion of normal constitution is neutrality to litmus. If the litmus is reddened the compound is "acid," or there is a "free acid" present; if reddened litmus is restored to blue there is an "alkali" present. I am not decrying the great value of the indications and teachings of litmus, if they are

* Abstract of a lecture delivered before the Chemists' Assistants' Association.

properly understood and interpreted, but merely pointing out the fallacy of relying implicitly on litmus as an indicator of chemical constitution. Thus, one may take two colourless liquids, one of which is without sensible effect on litmus, while the other turns reddened litmus to blue. On mixing the two the reaction will become strongly *acid*. Either we have converted an alkali into an acid, or the indicator is misleading us. The reaction which I have supposed to have occurred is this :—

$$Na_2HPO_4 + 3\ AgNO_3 = Ag_3PO_4 + 2\ NaNO_3 + HNO_3.$$
Alkaline. Neutral. Neutral. Neutral. Acid.

Hence there was nitric acid formed by the reaction, which quite accounts for the reddening of the litmus.

Except in certain cases, litmus is a very uncertain indicator of constitution, but of the natural colouring matters it is undoubtedly the most generally available, and in certain cases it is still the best indicator of neutrality which can be used. The end-reaction is not readily observed by gaslight, but when daylight is not available the neutral point can be ascertained very sharply by employing the monochromatic light of an incandescent sodium compound (such as a bead of sodium carbonate held in a loop of platinum wire in a bunsen flame). By this light, an acid solution of litmus appears nearly colourless, while the blue solution looks almost black.

Cochineal may be advantageously used in some cases, as the change from yellowish-red with acids to purple with alkalies is sharply marked, and the indicator is not affected by carbonic acid. It gives an alkaline reaction with the carbonates of the alkaline-earth metals, and hence the so-called "temporary hardness" of water can be rapidly and accurately ascertained by titration with cochineal and standard acid. But, as pointed out by R. T. Thomson, a radical objection to its general employment is the fact that, in presence of very small quantities of iron or aluminium, the pink colour, though modified, persistently remains after the neutral point has been passed.

Turmeric is an indicator which has received but little application. Its chief advantage is the possibility of using it in an alcoholic solution. Its most curious reaction is that with boric acid, which turns litmus a wine-red, but behaves with turmeric much like a free alkali.

The progress of organic research has of late years enriched the laboratory with a number of indicators of neutrality, which may in many instances advantageously replace the formerly universally employed litmus.

The use of these indicators requires discretion, and the first thing the user is likely to discover is that they cannot be employed indiscriminately as a substitute for litmus. But this circumstance, which at first sight might appear to be an obstacle to their use, is, in reality, one of their great recommendations; for they often give sharp end-reactions where the indications of litmus are hopelessly indefinite.

The great majority of indicators of neutrality, including the colouring matter of

litmus, are bodies of an acid character, and they owe their value to the fact that the solutions of their alkali-metal salts have a colour distinctly different from that of the free acid or hydrogen salt. When the acid properties of the colouring matter are very feeble, or, in other words, when its "affinity" for bases is very weak, very feeble acids will displace it from its salts, with the characteristic change of colour indicating the liberation of the colour-acid. Such an indicator will be available for the titration of very feeble acids, and we have it in the invaluable colour-acid, *phenolphthaleïn*, a body which in solution in the free state is practically colourless, but the soluble metallic salts of which have, in solution, a magnificent crimson-red colour. By means of phenolphthaleïn and caustic alkali we can titrate very feeble acids, and either in aqueous or alcoholic solution, as may be preferred. With phenolphthaleïn, acetic, benzoic, citric, tartaric, and other organic acids, can be titrated far more accurately and sharply than with litmus; and it is equally available for stearic, oleic, and other insoluble fatty acids. In these latter cases, however, the operation should be conducted in alcoholic solution; not merely because the acids are insoluble in water, but because water effects more or less decomposition of their salts (soaps). Thus, on titrating an alcoholic solution of oleic acid with caustic soda the end-reaction is perfectly sharp; but on adding water a marked pink colour is developed, indicating that a certain amount of decomposition has taken place, probably owing to the partial hydrolysis of the soap with formation of an acid oleate and free caustic alkali.

Phenolphthaleïn is also available for the titration of many feeble mineral acids, including hydrocyanic, carbonic and arsenious acids, and even sulphuretted hydrogen. An interesting demonstration that phenolphthaleïn is affected by carbonic acid is obtained by adding that indicator to water rendered faintly alkaline by caustic soda. On then blowing through the liquid, it becomes decolorised by the carbonic acid of the breath. But the very fact that carbonic acid reacts on the indicator shows that the standard alkali used for a titration must be caustic and free from carbonate. This is very difficult to insure in the case of caustic potash and soda, and ammonia cannot be employed with phenolphthaleïn. By far the best standard alkaline solution for use with phenolphthaleïn is decinormal baryta water, which, if clear, must necessarily be free from carbonate.

It may be set by any ordinary acid, but the compound to which I give the preference is the quadroxalate of potassium, a salt of the composition KHC_2O_4, $H_2C_2O_4 + 2$ aqua. It is prepared by making a saturated solution of recrystallised oxalic acid in water and filtering the liquid. One-fourth of the filtrate is then heated to boiling, and neutralised with pure potassium bicarbonate, employing litmus paper as the indicator of neutrality. This neutralised portion is then added to the main quantity, whereupon there is copious deposition of the quadroxalate in the form of granular crystals. This is filtered off, washed with a little cold water, and dried over sulphuric acid. It is perfectly permanent in the air, and in that respect presents a great advantage over oxalic acid. In using the quadroxalate for setting the standard baryta solution, about 0·25 gramme is exactly weighed and dissolved in a little warm water. Phenolphthaleïn (1-500 solution in proof spirit) is

then added, and the baryta water run in until the pink colour becomes permanent. During the first part of the titration the solution remains quite clear, but subsequently a white precipitate of barium oxalate is produced, and this forms an extremely delicate background for viewing the end of the reaction. In fact, it is distinctly advantageous to aim at the presence of a finely-divided white precipitate in the liquid, rather than to employ a white background to the vessel. Potassium bitartrate may be substituted for the acid oxalate, but it is difficult to obtain the salt perfectly pure.

In many cases phenolphthaleïn can be advantageously employed with an ethereal solution of the acid to be determined. Thus, suppose it be desired to determine the benzoic acid in a sample of paregoric suspected not to be of B.P. quality. 20 c.c. may be taken, rendered slightly alkaline to litmus, the spirit evaporated off, and the camphor and oil of anise extracted by agitation with ether. On adding hydrochloric acid to the separated aqueous liquid, benzoic acid will be precipitated, and on agitation with ether will be extracted. The ethereal solution is separated, washed with small quantities of water till the washings no longer appreciably redden litmus, and placed in a small cylinder together with about 5 c.c. of water to which a drop of phenolphthaleïn solution has been added. On now dropping in $\frac{N}{20}$ or $\frac{N}{50}$ caustic soda or baryta, and agitating well between each addition, the estimation of the benzoic acid can be readily and accurately effected. The meconic acid of the opium is dissolved more or less completely by the ether used for extracting the benzoic acid, but the proportion present is too small to interfere with the determination of the latter.

The foregoing method of titrating benzoic acid also finds an application in the process of assaying aconite alkaloids suggested by me. By its means the proportion of saponifiable alkaloids in as little as half a grain of material can be ascertained with a considerable approach to accuracy. This is an important improvement in practice on the method based on the same principle originally proposed by Dr. Alder Wright, whose experiments were made prior to the utilisation of phenolphthaleïn as an indicator, and on such large quantities of material as to render the process quite prohibitive in actual practice.

But although phenolphthaleïn reacts perfectly with such weak acids as carbonic and hydrocyanic, there are bodies of an acid character which have little or no action on it. This is the case with phenol and other bodies of that class, such as morphine, the molecule of which contains a hydroxyl group having a phenolic function, which enables it to form compounds with the alkalies, and is the cause of its solubility in caustic alkalies and lime water. I lay some stress on the behaviour of morphine with phenolphthaleïn, because it has been stated that morphine reacts as an acid to phenolphthaleïn, until one molecular weight of NaHO has been added for each molecular weight of morphine; or, in other words, in the proportion for the reaction :—

$$C_{17}H_{19}NO_2.OH + NaOH = C_{17}H_{19}NO_2.ONa + H_2O.$$

In consequence of this statement, I have submitted the behaviour of morphine with phenolphthaleïn to direct experiment. The end-reaction is not a sharp one, and appears

to be modified by the presence of alcohol and other conditions, but in all cases I found the acidity of morphine to phenolphthaleïn extremely trifling, and the caustic alkali required for the production of a pink colour was only a small fraction of that which would be required for the above reaction.

P. C. Plugge (*Arch. Pharm.* [3] xxv., 45) finds also that in titrating morphine hydrochloride with caustic alkali and phenolphthaleïn a red coloration makes its appearance *before* the end of the reaction (that is the neutralisation of the HCl), but states that a little experience enables the difficulty to be overcome.

It is evident, therefore, that morphine has a faint acid tendency, but the statement that it reacted quantitatively as an acid to phenolphthaleïn was a mistake, and I think there is little doubt that the behaviour of morphine to phenolphthaleïn was confused with that to Poirrier's soluble blue CLB. This colouring matter, not now manufactured, was found by M. R. Engel in 1886 (*Compt. rend.*, cii., 214, 262, 431), to be capable of being used as an indicator for the very weakest acids.

The concentrated solutions of the compounds KBO_2, K_3PO_4, K_3AsO_4, K_2PHO_3, K_2PHO_2, and K_2CO_3, are stated to have been found approximately neutral to this indicator. About 85 per cent. of the hydrogen of H_3PO_4 and H_3AsO_4 was indicated, so that the colouring matter could not be used for the actual titration of these acids. It is only to be expected that the salts of very feeble acids should readily suffer hydrolysis, especially the salts in which the last atom of hydrogen is replaced. Morphine, phenol, resorcin, and chloral all reacted as acids to Poirrier's blue, the last three being capable of accurate titration by means of it. Phenol and chloral acted as monobasic, and resorcin as a dibasic acid. Morphine did not give such good results, a quantity of caustic alkali being required somewhat in excess (24 c.c. against 20), of that corresponding to "the double phenol function." The meaning of this is apparently that Engel found at least 2NaHO to be required for $C_{17}H_{20}NO_3$. This result is interesting, but requires confirmation, as do other of Engel's observations. Engel found Poirrier's blue to be neutral to the hydroxyl group existing in monovalent alcohols (even when these were of tertiary constitution, like trimethylcarbinol and pinacone), but in strong solution polyvalent alcohols, such as glycerol, erythrol, and mannitol, showed an acid *tendency*, though they were not capable of being accurately titrated. Hydrocyanic acid could be determined by titration with Poirrier's blue, and glycocine, alanine and taurine also behaved as acids, but the end-reaction was indistinct.

It is interesting to observe that phenolphthaleïn and Poirrier's blue, which may be used as indicators for very feeble acids, are absolutely indifferent to the majority of the alkaloids and organic bases. Even aniline and pyridine, which have such strongly-marked basic characters, are perfectly neutral to phenolphthaleïn. The same is true of strychnine, quinine, aconitine, and, with the limitation already mentioned, morphine. Hence the salts of these bases, such as hydrochloride of aniline, sulphate of quinine, and nitrate of

aconitine*, can be titrated with caustic alkali and phenolphthaleïn, just as if the respective acids were in an uncombined state. According to E. Léger, cicutine and codeine are exceptions to the general rule of indifference of the alkaloids to phenolphthaleïn, and, according to P. C. Plugge, nicotine and conine also exhibit an alkaline reaction. A curious exception to the general behaviour of alkaloids is also presented by atropine and its isomers (as also homatropine), which in the free state strongly redden phenolphthaleïn. This property, however, does not exist in alcoholic solution, a fact which marks a curious distinction between these alkaloids and the mineral alkalies, the alcoholic solutions of which react perfectly with phenolphthaleïn.

One inconvenience is attached to the use of phenolphthaleïn as an indicator, which is that it is gradually decomposed by ammonia, and hence cannot be safely used for titrating that base, or in presence of its salts; but this fact being recognised in practice, it causes very little inconvenience. Nevertheless, "an indicator possessing the general properties of phenolphthaleïn, but not possessing this imperfection, is still a desideratum."

But if phenolphthaleïn and its allies indicate very feeble acids, it is evident that they fail as indicators of the majority of alkaloids, and other of the feebler bases. If we desire an indicator for weak bases we must look for a substance which has a fairly strong affinity for bases, and which shows by a change of colour that it has "met its affinity." Of all indicators of the sort hitherto proposed, the one which best answers the required purposes is the azo-dye known as *helianthin* or *methyl-orange*. This colouring matter is the sodium salt of the sulphonic acid of dimethyl-amido-azobenzone. Its solutions have a yellow colour, but the free acid is red. Hence, the addition of an acid sufficiently powerful to liberate the acid from its salts results in a change of colour from yellow to red. This change is sufficiently marked, though it does not approach the sensitiveness of phenolphthaleïn to alkaloids, and is not available in a strongly alcoholic liquid. The free acid of methyl-orange, which for convenience may be termed "helianthic acid," is only sparingly soluble, but is none of the weakest in its affinities. Hence, feeble acids like boric, carbonic, and hydrocyanic are *wholly* unable to decompose its salts; acetic and oxalic acid do so only imperfectly; while with sulphuric, hydrochloric, nitric, and thiosulphuric acids, complete decomposition ensues. With phosphoric acid, decomposition ceases rigidly with the formation of a compound analogous to Na_2HPO_4, which fact has been utilised by Mr. J. Hodgkin for the examination of glacial phosphoric acid.

The soluble acid calcium phosphate, containing $CaH_4(PO_4)_2$, which is the leading constituent of commercial "superphosphates," is neutral to methyl-orange, and hence any excess of acid can be readily determined. The neutrality of these acid phosphates to methyl-orange is in striking contrast to the behaviour of the sodium phosphates with phenolphthaleïn, with which indicator Na_2HPO_4 is neutral; while, according to Engel, with Poirrier's soluble blue, the compound Na_3PO_4 is approximately indifferent.

*Ordinary nitrate of aconitine is not a neutral salt. It contains $B_2(HNO_3)_3$.

Methyl-orange being totally indifferent to such weak acids as boric, carbonic, sulphydric, and arsenious, the alkaline borates, carbonates, sulphides and arsenites behave just like their equivalents of free alkali. With methyl-orange as an indicator, standard acids may be set with sodium carbonate or borax (the latter salt having been actually recommended as giving a solution absolutely permanent and without action on glass); and the "temporary hardness" of water and the "total alkali" of soda ash may be determined in a few minutes. All the alkaloids and organic bases of which the behaviour has hitherto been examined—except urea, caffeine, theobromine, and, perhaps, aniline—may be titrated with methyl-orange and a standard mineral acid, and with much greater facility than when litmus is used (phenolphthaleïn, as already stated, is inapplicable).

An indicator which in every respect (except its non-destruction by nitrous acid) behaves like methyl-orange is the colouring matter inappropriately named *lacmoid*. In the form of paper, especially, this is a very useful indicator, which may be used in cases where the deep colour of the solution prohibits the employment of helianthin.

(*To be continued.*)

The Determination of Sulphur in Coal by Eschka's method. F. Hundeshagen. (*Chem. Zeit.*, xvi., 1070, 1071.)—Eschka's method for determining sulphur is liable to give low results from the loss of part of the sulphur as volatile compounds. Even when more than the prescribed quantity of the mixture of magnesia and sodium carbonate is used, as much as six per cent. of the total sulphur may be lost, and this amount may be much exceeded if the mixture be damp and the heating rapid. The volatilisation of a portion of the sulphur can easily be recognised by holding a strip of lead paper over the crucible.

The improvement advocated by the author consists in substituting potassium carbonate for the sodium salt. The mixture used by him is composed of two parts of magnesia, and one part of calcined potassium carbonate. Two parts of this are taken for one of coal. The reaction is quicker than with sodium carbonate, it being completed in a quarter or half-an-hour. The results quoted are about 0·15 per cent. higher with brown coals containing about 2 per cent. of sulphur. The reason for the low results with sodium carbonate is that it becomes anhydrous and comparatively inert at a somewhat low temperature, and, further, that sodium sulphide is easily decomposed by moist carbonic acid, the contrary, in each case, holding good for potassium carbonate. The absorption of sulphur is also facilitated by the formation of a certain quantity of potassium hydrate, under the conjoined influence of magnesia and moisture, there being but little tendency to form sodium hydrate under like conditions.

B. B.

To Stain Bacteria in Fatty substances such as Milk. (*Centralblatt f. Bakteriol. u. Parasiten Kunde*, xi. 10, through *Royal Microscopical Society's Journal*, 1892, p. 291) —A loopful of milk and a loopful of distilled water are mixed on a cover-glass, dried, and fixed at a gentle heat. The cover-glass is then placed in a watch-glass containing chloroform-methylene-blue (made by mixing 12 to 15 drops of a saturated alcoholic solution of methylene-blue and 3 to 4 c.c. of chloroform). In this solution the cover-glass is moved to and fro for 4 to 6 minutes. The chloroform is then allowed to evaporate, the preparation washed with, and examined in, water. In fresh milk and cream the bacteria only are stained, but, if curdled, the flakes of casein are dyed a pale blue. This does not, however, interfere with the distinctness of the bacteria, which are stained deep blue.

F. H. P. C.

Estimation of Sulphuric Acid in Sulphates. A. v. Asboth. (*Chem. Zeit.* 1892, xvi. 922.)—With reference to Stolle's method (THE ANALYST, xvii. 115), Asboth points out that a solution of barium chromate in hydrochloric acid begins to evolve chlorine very soon after it has been made, some of the barium chromate being, of course, simultaneously decomposed into barium and chromium chlorides. Such a solution was found to give very erroneous results, when used 24 hours after it had been made. If the barium chromate were dissolved in hydrochloric acid immediately before each determination, error might be avoided; but much of the convenience of the process would thus be sacrificed.

A. G. B.

The Microscopic Examination of Butter by Polarised Light. (*Collected from the original sources by H. D. Richmond.*)—The use of the microscope for detecting foreign fats in butter was first proposed by Hassal; it depends on the broad principle that fats, which have been fused and allowed to cool, contain crystals, which rotate somewhat a ray of polarized light, while butter fat does not. Campbell Brown (*Chem. News*, xxviii. 1), in 1873, and in 1874, Hehner and Angell, in "Butter and its Adulterations," dwelt upon this method, and give figures, showing the difference in appearance of pure and adulterated butter when microscopically examined by polarized light; Hehner and Angell, however, recognize the fact that pure butters sometimes give similar appearances to those of artificial samples. Mylius (*Ber.* xii. 270), in 1878, and Rabot (*Industrie Laitière*, 1885, No. 34, 271), in 1885, have discussed the method. The most complete memoir on the subject is by Taylor, who studied the subject from 1876 till 1885, presented to the Society of American Microscopists, at their Cleveland meeting in 1885. His results are scattered through the *Scientific American*, and the *Microscopic Journal*, during those years, and are collected in the *Industrie Laitière*, 1881, 47, 370, and the *Milch-Zeitung*, 1882, 2, 27, and 1885, 47, 744. Taylor is, on the whole, favourable to the method. Sell concludes (*Ueber Kunstbutter*, 63, *Berlin*, 1886), that there is not a specific difference between the crystals of butter and

those of beef fat, &c., on microscopic examination, because it is possible to produce conditions under which different kinds of fat behave in the same manner; he speaks highly of Taylor's work, from a scientific point of view, but denies to it a practical importance. Besana, in a recent work (*Sui metodi atti a distinguere il burro artificiale dal burro naturale*), attaches no importance to the microscopic examination of butter. Quite recently, Pouchet (*J. d'Agriculture pratique*, 1892, 1, 4), speaks highly of the method, the discovery of which he attributes to Pennetier, in 1888; his opinion has been widely published in English and French journals, both trade organs, and general periodicals. Pizzi (*Staz. Sper. Ag. Ital.* 1892, 131), has examined sundry genuine butters and margarines, and mixtures containing ten, five, and one per cent. of margarine; he publishes a plate, showing the appearance of these when examined with a selenite plate under polarized light, which shows that even $1^{o}/_{o}$ gives faintly the characteristic colours of crystalline fats; he alleges that Sell (*loc. cit.*), does not state what are the conditions under which different kinds of fat behave in the same manner. Both Pouchet and Pizzi have done no more than establish the broad principle enounced by Hehner and Angell, as they do not appear to have examined any considerable number of butters. It is significant that Hehner, who may be regarded as one of the originators of the methods, has, in common with most other English analysts, discarded the method. At a recent meeting of the Society of Public Analysts, Stokes stated that he was always able to detect margarine by the microscope, while he not unfrequently found the same appearances in butter; he condemned the use of a selenite plate; his first statement was, however, doubted by Cassal and others.

The method adopted by all experimenters was practically the same, viz., to crush a small portion of the butter between two microscope slides, and to examine it with a low power ($\frac{1}{2}$ to 1 inch), under polarized light; with pure butters, no definite change was visible; the presence of margarine or fused fats was shown by the light passing in certain portions of the field, giving a brilliant appearance, where no selenite plate was used, and a play of colours where it was introduced.

H. D. R.

The Acetic Acid Test for Fats. F. Jean. (*Industrie Laitière*, 1892. *No.* 26 205). The acetic acid used was glacial acetic acid, to which enough water had been added to raise the density to 1·0565 at 15°C.

Three c.c. of oil or fat are introduced into a tube 1 c.m. in diameter, and graduated in $\frac{1}{10}$ of a c.c.; the tube is placed in a water bath at 50°C., and the volume of the fat accurately adjusted to 3 c.c. 3 c.c. of acetic acid, measured at a temperature of 22°C., are then poured in from a pipette. The fat and the acetic acid are shaken several times to ensure complete admixture, and the layers are allowed to separate completely in the water bath at 50°. By subtracting the quantity of acetic acid from 3, and multiplying by 33·3, the percentage of acetic acid dissolved by the fat is obtained.

In this way numerous samples of butter of various sources were found to dissolve 63·33 per cent. acetic acid; 4 butters from Touraine however dissolved 73 per cent.

Maize, castor, cocoa-nut and mineral oils dissolved 100 per cent. of acetic acid; Indian poppy oil, 63·3; beech nut oil, 53·3; and camelina, nut, olive, Arachis (earth nut), neats foot, palm, sweet almond, poppy, radish, and rape oils, dissolved from 30 per cent. to 43·7 per cent.; margarine from 26·7 per cent. to 40 per cent; tallow, 26·7 per cent., and rosin oil nothing.

The author applies this test in conjunction with the reading of his oleorefractometer, and the Reichert-Wollny figure for the detection of adulteration in butter.

As examples of its use he gives figures.

Description of Butters.	Oleorefractometric Reading.	Solubility of Acetic Acid.	R.-W. Figure.
Normandy (pure) ..	—30	63·33	29·25
Rennes („) ..	—29	63·33	27·5
Touraine („) ..	—36	73·0	31·42
Brittany (suspicious) ..	—25	60·0	24·7
Ardennes (suspicious) ..	—27	58·33	—
Indre-et-Loire (suspicious)	—26	56·66	25·75
Rennes, salt (adulterated)	—25	60·0	23·98
„ (suspicious) ..	—25	60·0	—
Brittany (suspicious) ..	—25	60·0	22·99
Rennes (suspicious) ..	—26	60·0	22·0
Brittany, salt (suspicious)	—25	60·0	23·65
Isigny + 10 % cocoa-nut oil	—33	66·66	26·8
„ + 15 % „	—34 (strong)	90·0	—
„ + 28 % „	—36	96·0	24·13
„ + margarine ..	—24	53·0	—

The author from these figures concludes that the three methods are enough to distinguish adulteration in butter, even with cocoa-nut oil. Thus the Isigny butter, adulterated with cocoa-nut oil, cannot be confounded with the Touraine butter, as though the oleorefractometric reading and the solubility of acetic acid increase, the Reichert-Wollny figure is lowered.

H. D. R.

A Sensitive Reaction for Albumin in Urine. By E. Spiegler. (*Ber.*, 1892, 25, 375—378). The urine is acidified with acetic acid, and cautiously dropped from a pipette into a solution of mercuric chloride (8 parts), tartaric acid (4 parts), and sugar (20 parts), in water (200 parts), when the presence of albumin is indicated by the formation of a sharp, white ring at the point of contact of the two liquids. The solution prepared as above has a specific gravity of 1·06; the sugar plays no part in the reaction, but is simply added to raise the density of the solution, and in testing strong diabetic

urines, a further addition of sugar is necessary to prevent its mixing with them. Peptone does not give the reaction, but propeptone does give it. One part of albumin in 150,000 is readily detected; whilst by allowing the test to stand for a few minutes, one part in 225,000 can be detected, whereas the sensitiveness of the ferrocyanide reaction has a limit of one part in 50,000. A. R. L.

The Purity of Olive Oil. F. Lengfeld and L. Paparelli. (*Rev. Internat. des Falsificat.*, 1892, v., 98.)—The authors have examined certain samples of Californian olive oil, with the results given in the table below. Samples of a few other oils, namely, cotton seed and white and black mustard, were also tested.

	No. of Oil.	Iodine Absorption.	Rise of Temp. deg. C.	Fatty Acids. per cent.	M.P. of Fatty Acids. deg. C.
Californian.	1.	80·80	37	94·5	Below 28
	2.	77·28	35	94·0	28—30
	3.	87·15	39·5	96·05	Below 28
	4.	83·35	37·5	95·50	,,
	5.	88·68	41	95·65	28—30
	6.	81·45	38	95·93	Below 28
	7.	79·50	36	94·80	,,
	8.	79·53	34·5	95·92	,,
	9.	78·42	33·5	95·87	,,
	10.	78·45	—	95·68	,,
	11.	85·44	36·5	95·98	,,
Unknown origin.	12.	81·70	34	95·77	Below 28
	13.	81·50	35	95·86	,,
	14.	78·52	34	94·84	,,
	15.	78·51	33·5	95·97	,,
	16.	105·40	—	96·59	35—36
"Union Salad Oil"	17.	105·30	72	96·66	35—36
Cotton-seed	18.	107·00	79	96·17	37—38
White Mustard	19.	97·68	49·5	96·70	34—36
Black Mustard	20.	103·07	58·5	—	34—36

The samples numbered from 1 to 11 inclusive were Californian olive oil, the purity of which the authors consider beyond question; those from 12 to 16 were of unknown origin. All the foregoing, with the exception of No. 16, gave no reaction with Bechi's, Hauchecorne's, or Brullé's reagents. No. 16 reacted with all three, as did also No. 17, which was sold under the title of Union Salad Oil. The sample of cotton-seed oil gave a reaction in each case, while the two samples of mustard oil gave no reaction with the Bechi test, but were detected by the other two reagents. B. B.

Analysis of Sulphides. P. Jannasch, V. Wasowicz, K. Aschoff, and T. Bickes (*Jour. f. Prakt. Chem.*, 1892, XLV., 94-114.)

(1.) *Molybdenum Glance.*—The finely-powdered mineral is heated in a platinum boat in a combustion tube through which a current of oxygen is passed. The temperature is kept low at first and gradually raised, but must not be sufficiently high to volatilise molybdic acid. The evolved vapour of "sulphuric acid" and sulphurous anhydride are absorbed in a 3 per cent. solution of hydrogen dioxide. When the colour of the contents of the boat have passed to a greyish white, with perhaps a greenish tinge, the decomposition is complete, and the boat is withdrawn. The tube is washed with hot water and the washings added to the hydrogen dioxide in the absorption vessels. The mixed liquids are evaporated to 100 c.c., acidified with hydrochloric acid, and precipitated with barium chloride, with the usual precautions, for estimation of the sulphuric acid. To determine the molybdic acid, the boat, with its contents, is weighed, and the latter dissolved in ammonia, when as a rule a gangue, consisting of a reddish powder, remains undissolved. This is filtered off, washed with ammonia, and treated with hydrochloric acid for the determination of iron and silica by the usual methods. The ammoniacal solution is evaporated until all free ammonia has been expelled and precipitated with a solution of mercurous nitrate. After 24 hours the precipitate is filtered, washed with a dilute solution of mercurous nitrate, dried at 110°, and removed as far as possible from the filter into a Rose's crucible, that which adheres to the filter being dissolved in dilute nitric acid and added to the crucible, from which the liquid is then evaporated on the water-bath. The mercurous molybdate is finally reduced in hydrogen, at first over an ordinary gas flame and finally over the blow-pipe, and the molybdenum weighed. Two hours heating is frequently necessary before the weight is constant.

(2.) *Realgar and Orpiment.*—The decomposition is effected as in the case of molybdenum glance, but all the arsenic passes into the absorption vessels. The gangue can thus be weighed directly, as the residue in the boat. The hydrogen dioxide solution is concentrated to about 140 c.c., excess of ammonia is added, followed, when the liquid is cold, by magnesia mixture, made with magnesium chloride, a large excess being avoided. After 24 hours the precipitate is filtered, washed with ammonia, dissolved in hydrochloric acid, and again precipitated with ammonia and another drop or two of magnesia mixture. The ppt. is finally dried at 100°, and transferred to a Rose's crucible, that adhering to the paper being dissolved in dilute nitric acid, added to the crucible, and the liquid evaporated. Finally the crucible is heated at a gradually increasing temperature to redness, a current of oxygen being passed the while. The sulphuric acid is determined in the original filtrate from the ammonium magnesium arsenate after evaporating off the ammonia and acidifying with hydrochloric acid.

(3.) *Galena.*—The powdered sample is heated to dark redness in a boat in a combustion tube, through which a stream of oxygen carrying nitric acid vapour (which has been taken up by the oxygen in bubbling through fuming nitric acid) is passed. Hydrogen

dioxide is again used as the absorbent. After an hour a saturated solution of ammonium carbonate, kept warm and containing undissolved ammonium carbonate, and air are substituted for the nitric acid and oxygen respectively; the temperature of the tube is once more raised to redness and kept there until the contents of the boat have become a bright yellow liquid consisting of molten lead oxide, which generally happens in half an hour. The boat is withdrawn from the cooled tube, and the latter is washed with hot water, the washings being mixed with the absorbing liquid. The sulphuric acid is determined in the mixed liquids in the usual way. The lead oxide is dissolved from the boat in nitric acid, and determined as usual, if required. Air has to be substituted for oxygen when ammonium carbonate is used, to avoid explosions.

The authors have devised other methods for analysing galena in the wet way. The mineral is oxidised with strong nitric acid, any separated sulphur being oxidised by the addition of bromine; the mass is evaporated to dryness and, lest any lead bromate be formed, moistened with strong hydrochloric acid, and again evaporated three or four times. The lead sulphate is then dissolved in sodium hydroxide, filtered from gangue, and the lead precipitated from the solution as peroxide, either by chlorine or bromine, in the cold; or the lead sulphate may be dissolved in ammoniacal ammonium acetate, and precipitated by hydrogen dioxide in the cold. The lead peroxide may be dissolved in nitric acid after the addition of a little alcohol, and the lead weighed as sulphate. The sulphuric acid is determined in the filtrate from the peroxide.

The authors also find that it is possible to determine the sulphur and lead in galena by heating the mineral in a stream of air laden with bromine vapour. The sulphur passes on, apparently, as sulphur bromide, and the lead remains as lead bromide, which is non-volatile at the temperature necessary, namely, the melting point of the bromide.

A. G. B.

The Occurrence of Metallic Lead in Tartaric Acid. Guillot. (*J. Pharm. Chim.*, 1892, xxv., 541, through *Chem. Zeit.*)—The author has found lead in samples of tartaric acid intended for pharmaceutical use. (See preceding Abstract.) Such tartaric acid did not wholly dissolve in 90% alcohol, nor in water, and contained 0·514% of ash. The aqueous solution of the acid, when saturated with ammonia and made feebly acid with hydrochloric acid, gave a precipitate of lead sulphide with sulphuretted hydrogen. 0·0528 grm. of lead was obtained from the solution of 1 kilo of the acid. The residue left on dissolving 1 kilo of the acid in boiling water, consisted of fragments of wood, crystals of calcium sulphate and metallic lead. The latter were picked out by hand and weighed; the quantity was 0·0626 grms. The lead is derived from the wooden lead-lined vessels used in the manufacture of the acid. B. B.

Lead in Tartaric Acid. C. Buchel. (*J. Pharm. Chem.*, 1892, xxv., 540, through *Chem. Zeit.*)—The author has found combined and even free lead in all the samples of tartaric acid, both of French and foreign make, that he has examined. B. B.

The Impossibility of completely separating Barium as Sulphate from strong solutions of Strontium Salts. S. Cannepin. (*L'Union Pharm.*, through *Chem. Zeit.*)—The author finds, in spite of the statements to the contrary of Barthe and Falières, that it is impossible to separate barium completely as sulphate from concentrated solutions of strontium salts, as there is a limit to the re-action, beyond which the precipitated barium sulphate gives up as much barium to the strontium solution as the calcium sulphate or strontium sulphate, used as a precipitant, throws down. Complete separation can be effected by the use of strontium chromate, for which potassium bichromate may be conveniently substituted, provided the presence of potassium be unobjectionable. B. B.

Hübl's Iodine Absorption Method. D. Holde. (*Chem. Zeit.*, 1892, XVI., 1176—1178.)—The author has stated in previous communications that the Hübl method, as usually carried out, does not give the highest or concordant results. He has come to the conclusion that for most of the oils he has examined, an excess of 65 to 75 per cent. of iodine is necessary, and that the iodine solution should be freshly prepared. Some time after the publication of these precautions, Fahrion published some improvements of the method, in which the author's suggested large excess of iodine was adopted, and the plan of keeping the solutions of mercuric chloride and iodine separate recommended. Although economical, this plan should, according to Benedikt, with whom the author concurs, be modified by mixing the solutions at least two days before use, as the alteration in strength of the solution immediately after mixing is apt to be great. The differences due to variations in the method of standardising the iodine solution are shown by the following example: 0·2 gram of an oil with an iodine absorption of 100 was dissolved in chloroform in the usual way, 50 c.c. of an iodine solution, two days old, added, and the reaction allowed to proceed for two hours. Two blanks were used, one at the beginning, the other at the end of the period of absorption. According to the former the amount of iodine present was 1·008 gramme, while the latter gave 1·000 gramme, and the titration of the oil showed that 0·800 gramme of iodine remained unabsorbed. According to the former method, therefore, the oil absorbed 0·208 gramme of I., that is, it had an iodine absorption of 104, while taking the latter figure, it absorbed 0·200 gramme, and its iodine absorption was therefore 100. Strictly speaking, the value, 1·000 gramme, got by the end titration is somewhat too low, as a part of the iodine would have been absorbed by the oil before it has ceased to be free and active by spontaneous loss of strength of the Hübl solution, so that the real correction may be taken as 0·007 instead of 0·008 gramme. Practically however, this makes little difference, the figure becoming 100·5 instead of 100, provided that the excess of iodine used be so large that the quantity remaining free throughout the operation is comparable with the total amount contained in the blank.

The difference between the values got by standardising the Hübl solution at the beginning and end of the operation is less than given above, when the solution is more than two days old, and therefore, alters in strength correspondingly more slowly.

It may be said, for the sake of clearness, that the author and Benedikt reckon the excess of iodine prescribed on the total amount contained in the quantity of solution used either for the blank or for adding to the oil, while Fahrion refers his percentage to the amount of iodine absorbed by the oil. Thus an excess 50 per cent in the phraseology of the former is equal to 100 per cent. in that of the latter.

The considerable variations that may arise from using too small an excess of iodine and the differences displayed in this respect by different oils, are exhibited in the following table :—

Kind of oil and Solution used.	No. of C.C.'s of Iodine solution.	Excess of Iodine calculated on total iodine used.	Iodine number
Linseed oil (1) (weak I solution)	30	50 per cent.	158·8
	40	58 ,,	164·8
	50	65 ,,	169·4
	60	70 ,,	172·1
	70	76 ,,	173·0
	80	78·1 ,,	173·1
Linseed oil (1) (fresh I solution)	30	58 ,,	167·2
	40	66 ,,	171·2
	60	78 ,,	175·1
	70	81 ,,	175·1
	80	83 ,,	174·4
Walnut (1) (fresh I solution)	20	50 ,,	136·5
	25	60 ,,	135·3
	40	74 ,,	136·2
Rape oil (1)	17	44 ,,	97·6
	20	57 ,,	98·8
	35	78 ,,	99·7
	45	82 ,,	100·3
	55	84 ,,	100·3

With linseed oil and rape oil an excess of 75 per cent. of iodine is, therefore, necessary. With walnut oil a smaller excess suffices.

The author, in conclusion, insists on the necessity of observing other precautions such as exactitude of reading the burette and measuring the Hübl solution, for which he appears to use a burette. In the case of titrating a large number of samples he makes a blank experiment at the beginning and end of the titration, and calculates therefrom the exact value of the solution at the moment each sample is being titrated. B. B.

(Note by Abstractor.—The majority of the author's difficulties and the manifold devices to which he has been driven to circumvent them, appear to arise from the short time allowed for the absorption (two hours), which should be at least trebled to insure the completion of the reaction.)